

Effect of Sonication on Phase Transition Temperature of Cholesteryl Oleyl Carbonate

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Abstract – Cholesteryl oleyl carbonate (COC) was dissolved in chloroform and sonicated at different times (60, 120, 300, 900 and 1500 s). In order to calculate isentropic compressibility (κ_s) of prepared solutions, the density (ρ) and speed of sound (u) values were measured using a density and sound velocity meter at different temperatures (between 288.0 and 318.0 K). COC liquid crystals (LCs) were coated onto glass substrates by spin coating technique using the prepared un-sonicated and sonicated COC solutions. The images of all the COC LCs were by a polarizing optical microscopy (POM) with integrating temperature apparatus in range of 288.0 and 318.0 K. The phase transition temperatures (T_p) of the prepared COC were determined by means of the plotted κ_s vs. T graphs and POM images. The phase transition behavior was analyzed by the comparison of these results in terms of sonication time. It was observed that low sonication times (60 and 120 s) caused to the high T_p value.

Keywords – Liquid Crystals, Cholesteryl Oleyl Carbonate, Sonication, Isentropic Compressibility, Phase Transition.

I. INTRODUCTION

Liquid crystals (LCs) are interesting and extraordinary materials that sometimes have properties of conventional liquids and sometimes those of solid crystals. The interest in liquid crystals (LCs) has recently started to increase, and the reason for this increase is the high use of them, as well as a great commercial curiosity of them. LCs with high sensitivity to various external influences, especially thermal, electrical and magnetic fields, flows, deformations, surfaces, etc. have great application potential in science, technology and industry. These advanced technological materials are used in cosmetics, microelectronics, optoelectronics, information recording and reading systems as indicator, indicator and multimetric elements, as well as in thermography and medical diagnostics [1-4]. Digital clocks, calculators, television screens are

often used in many areas such as smectic and nematic liquid crystals [5-8].

LCs have many mesophases, and exhibit remarkable physical and physico-chemical features. Researchers have focused on liquid crystalline phase transition due to their established importance in field of applications for a few decades [9-12]. It was reported some results about the variations in density and thermal expansivity, which related to the transition from the nematic to isotropic phase [13-15]. However, isentropic compressibility may be used to determine the phase transitions and may give more clear information molecular about the studied structures, when compare to density measurements. Lin et. al [16] reported that the phase transition temperature of COC was investigated by a differential scanning calorimeter (DSC). During heating, they found that phase transition

temperature of COC from smectic to cholesteric is at 291.5 K, and phase transition temperature of COC from cholesteric to isotropic is at 310 K, whereas during cooling, these temperatures are 308.3 and 289.0 Chuealee et. al [17] reported that the endothermic peaks at 293.2 and 309.2 K corresponded to phase transition temperatures of COC from DSC measurements. Martinez-Felipe et. al [18] performed DSC measurements of COC, and found that phase transition temperature from smectic to cholesteric is at 295.7 K.

Since cholesteric LCs are thermotropic liquid crystals, they are used in temperature sensitive devices, medical applications, sensor usage, temperature measurement studies, cosmetics and decoration. Among them of cholesteryl oleyl carbonate (COC) is a liquid crystal material forming cholesteric LCs with helical structure. Since this structure is thermally responsive to changing reflective colors, for example, they are applicable for liquid crystal thermometers [19-21].

In the early 2000s, some reports have much attention about ultrasonic effects on crystallization. For example, the ultrasound has been reported to both speed up and diminish agglomeration [22-24]. In addition, it was investigated that the propagation of ultrasonic waves in liquids gives an information to molecular structure and the surrounding molecules [25, 26].

The goal of this work was to investigate the effects of sonication time on the phase transition for COC in chloroform. The phase transition temperature (T_p) was determined by means of the isentropic compressibility data and using polarizing optical microscopy (POM). Therefore, both applying ultrasound waves to the solution to prepare LCs and investigating the phase transition in terms of sonication time will be a first work in the literature.

II. MATERIALS AND METHOD

A. Preparation of the sonicated COC solutions and COC LCs

The chemicals cholesteryl oleyl carbonate (COC) and chloroform were purchased commercially. The formulas, suppliers, and mass fractions of the purchased chemicals and sample codes are given in Table 1. Phase transition temperatures of COC are presented in Table 2 in literature.

Table 1. Formula, suppliers, mass fraction purity of the chemicals and sample codes.

Component	Formula	Suppliers	Mass fraction
Cholesteryl	$C_{46}H_{80}O_3$	Acros	>0.990
Chloroform	$CHCl_3$	Merck	0.990-
Sonication	Sample Codes		
0	COC-0		
60	COC-1		
120	COC-2		
300	COC-5		
900	COC-15		
1500	COC-25		

Table 2. Phase transition temperatures of COC

C-Sm	T_p (K)		Method
	Sm-Ch	Ch-I	
300.2	273.2	310.7	Dilatometre
[27]	[27]	[27]	DTA
299.9	293.2	307.2	DSC
[28]	[28]	[28]	Optical
	286.2	308.8	DSC
	[29]	[29]	Optical
	297.2	313.2	Optical
	[30]	[30]	
	289.5	301.2	
	[31]	[31]	
	298.2	308.2	
	[32]	[32]	
	290.2	301.2	
	[33]	[33]	

C -crystalline, Sm- smectic, Ch- cholesteric, I -isotropic phases, DTA- Differential Thermal Analysis, DSC- Differential Scanning Calorimeter

Both chemicals were used directly without further purification (purity >99.9%). In order to prepare COC solutions, the weight ratios of mixture (COC:chloroform) were adjusted as 1:19. Sonication was applied to 10 ml of mixture in a glass vessel using a 20 kHz 700 W ultrasonic horn (QSONICA Q700 Sonicators) at an amplitude of

50% for 60, 120, 300, 900 and 1500 seconds. During the sonication, the temperature was kept constant at 296.15 K, using a cooling jacket. The prepared solutions were coded and the codes were given in Table 3. The schematic sonication set-up is given in Fig. 1.

A layer of COC LCs was prepared by spin coating technique using a spin coater (Laurell WS-400B-6NPP/LITE). The prepared un-sonicated (or sonicated) COC solution was dropped onto pre-cleaned glass substrate vacuumed on sample holder. The spin speed and time were selected 500 rpm and 30 s, respectively. Surface images of the coated COC LCs were taken immediately using POM with increased temperature from 298.15 K to nearly 50 K.

B. Characterization equipment

The density (ρ) and speed of sound (u) values for COC solutions were directly measured with the pulsed excitation method using an ANTON PAAR DSA-5000 measurement system. Temperature was automatically kept constant within ± 0.01 K. The ρ and u values for all the prepared COC solutions were carried out in the temperature between 288.15 and 318.15 K. The air and double-distilled water were used for calibration the apparatus. The uncertainties in ρ and u measurements were within $\pm 1.10^{-2}$ kg.m⁻³ and ± 0.5 m s⁻¹, respectively. The reproducibility of the measurements was found to be within 1.10^{-3} kg.m⁻³ and 0.1 m.s⁻¹ for ρ and u , respectively. The texture of the liquid-crystalline phase of the prepared COC LCs was performed with a POM (Nikon Eclipse 80i). POM was integrated with a water circulation bath and a temperature controller.

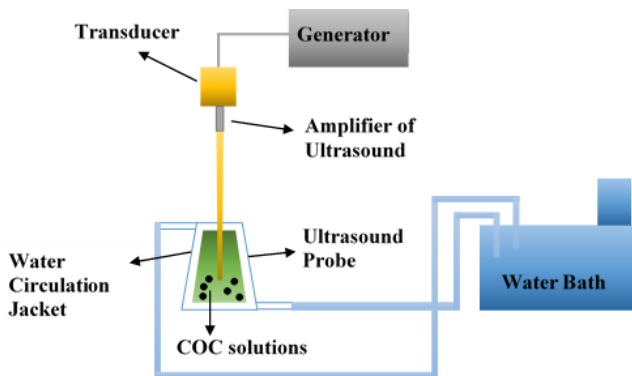


Fig. 1 The schematic sonication set-up.

III. RESULTS AND DISCUSSION

The plots of ρ -T and u -T for COC in chloroform at atmospheric pressure are given in Figs. 2 and 3, respectively. It can be seen that ρ and u values decrease with increasing temperature. The isentropic compressibility (κ_s) values were calculated from the measured ρ and u values, using the Laplace equation given below,

$$\kappa_s = \frac{1}{\rho u^2} \tag{1}$$

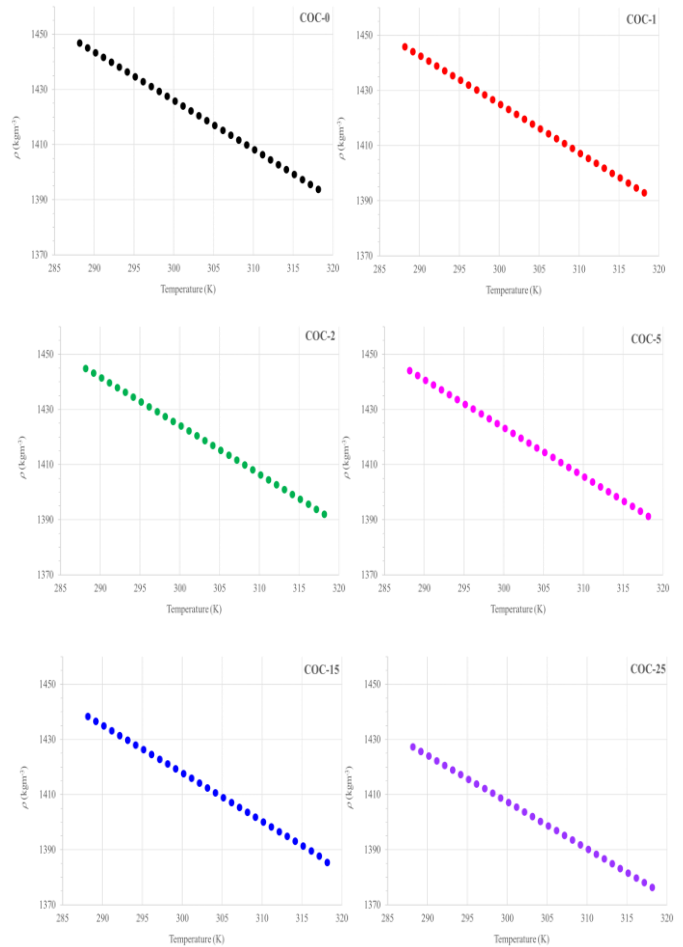


Fig. 3 u values of all the prepared COC solutions as a function of temperature.

Fig. 4 presents the calculated κ_s values for COC solutions as a function of temperature. The intersection method and Gauss method were used to determine the phase transition temperature (T_p) values of COC solutions. In the first method; there are two linear regions in all the plots, and the intersection point of two linear fits enabled T_p to be determined. The T_p value corresponds to the x -axis value of interception point. Two linear fits and intersection points for COC solutions are shown in

Fig. 4, and determined T_p values COC solutions are given in Table 2. In the second method; the plotted κ_s - T graphs can be analysed using Gaussian fitting. The minimum of the inverted Gaussian corresponds to points of maximum variation, and coincides with the T_p . These fitting curves are presented in Fig. 4, and the determined T_p values COC solutions are given in Table 3. The transition temperature (305.0) of COC (sonicated 120 s) was found to be higher than that of the unsonicated sample (which is the transition temperature, 296.4 K). The highest T_p (305.0 K) values were observed for the COC which were sonicated for 120 s. Ultrasonic waves are applied through the crystallization process. Effect of operating variables on expose time of ultrasound of crystallization of COC have been surveyed relating to crystal size distribution and their morphology. Continuous ultrasound produces many nuclei resulting in small crystals. The isentropic compressibility (κ_s) values are decreased from the smectic phase to the isotropic phase, however at the transition temperature it takes the high value.

When an LC material is placed on a substrate, is heated and viewed using a POM, characteristic of textures for each temperature can be seen. Therefore, the T_p values of COC LCs were also determined by means of POM. Figs. 5-10 show the POM images of the COC LCs for different temperatures (magnification at 20x). It is clear from these figures that there is a dramatic modification in the texture of the samples with the change in temperatures. From the first POM images of each COC LCs (Figs. 5.a-10.a), it can be seen typical focal conic textures observed for smectic phases. The smectic phase is the phases in which the molecules are arranged into "layers" in addition to being oriented along a particular axis, and which are observed at lower temperatures than the nematic phase [2]. Figure 5.b. shows the textures of the cholesteric phase. This phase was observed only in un-sonicated COC LC. When looking at the second of the POM images (Figs. 6.b-10.b), it can be seen that all of them are in the same textures. It can be said that this texture belongs to the isotropic phase and that the sonicated COC LCs have transitioned from the smectic phase to the isotropic phase. From these images, it can be said that sonication reduces the transition temperature to isotropic phase. Using these images, the T_p values were determined and

given in Table 3. The highest T_p values were observed for the LCs which were sonicated for 60 and 120 s (Figs. 6 and 7).

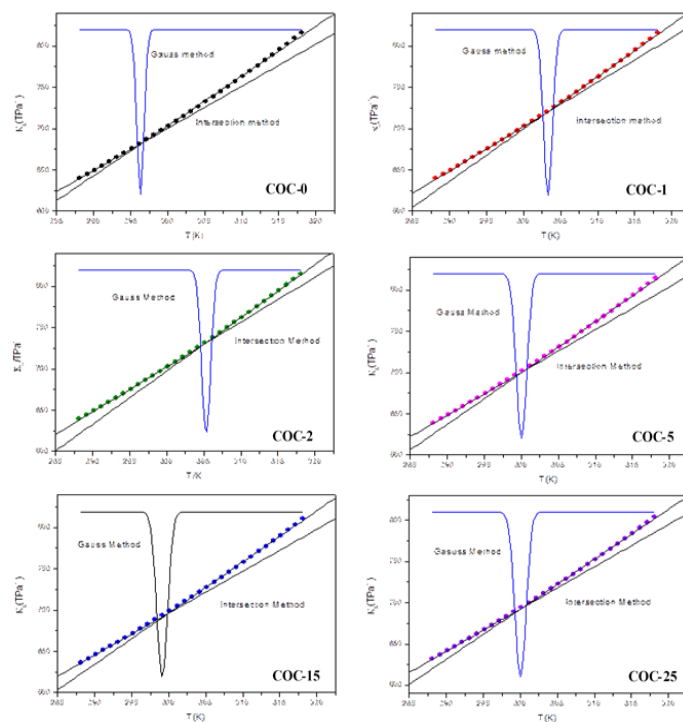


Fig. 4 The calculated κ_s values of all the prepared COC solutions as a function of temperature.

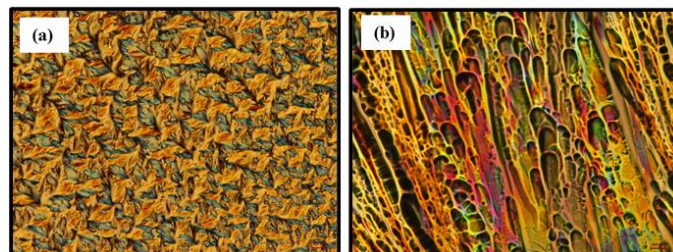


Fig. 5 POM images for LC of COC-0 at (a) 294.9 K (b) 296.1 K.

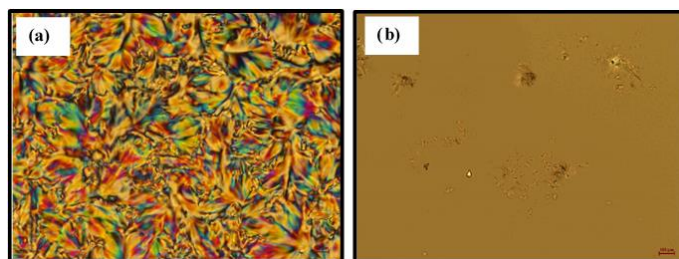


Fig. 6 POM images for LC of COC-1 at (a) 297.2 K and (b) 303.2 K.

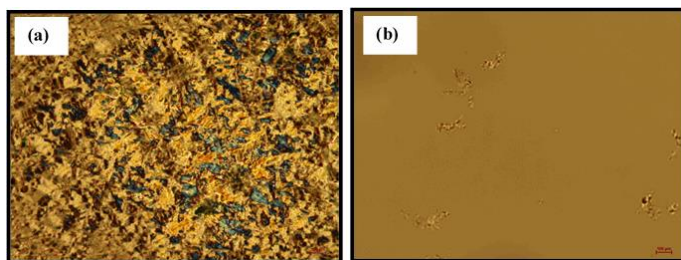


Fig. 7 POM images for LC of COC-2 at (a) 295.3K and (b) 304.9 K.

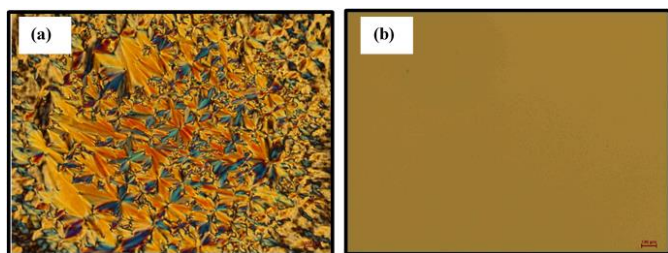


Fig. 8 POM images for LC of COC-5 at (a) 296.7 K and (b) 298.8 K.

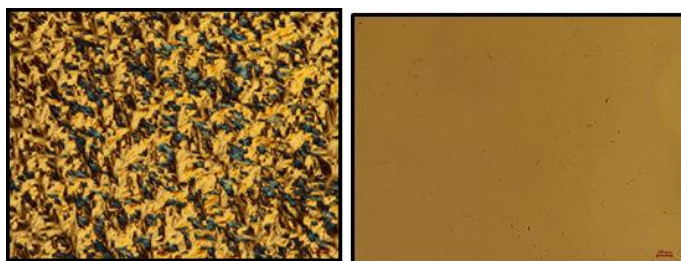


Fig. 9 POM images for LC of COC-15 at (a) 294.1 K and (b) 298.7 K.

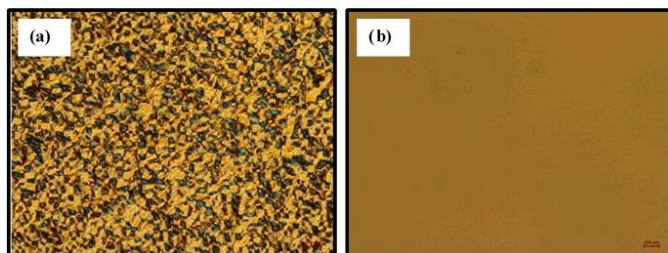


Fig. 10 POM images for LC of COC-25 at (a) 293.0 K and (b) 296.2 K.

Fig. 11 presents the comparison of the T_p values obtained by different methods (POM, intersection method and Gauss method). It can be seen that the T_p values determined by three methods are in good agreement. These results indicate that κ_s data can be used for the determination of T_p value with the highest accuracy. The results are good agreement with reports in the available literatures [18, 27-33].

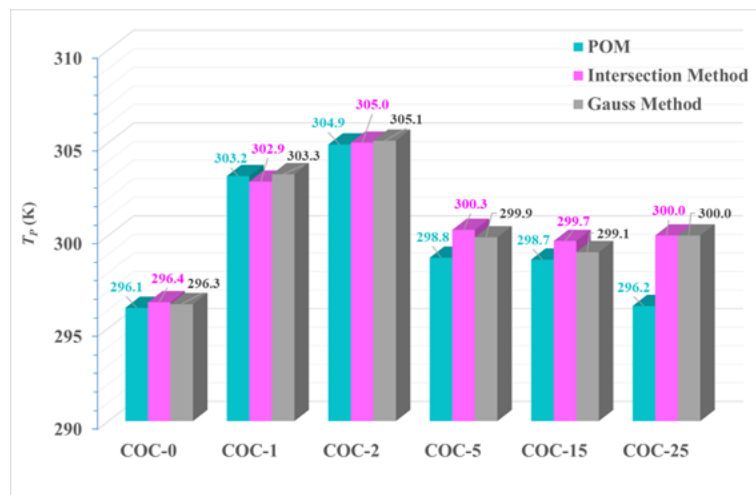


Fig. 11 A comparison of the determined T_p values using different methods.

IV. CONCLUSION

In this work, the T_p values for the COC in chloroform were determined successfully by using the calculated κ_s data from the measured ρ and u values at various temperatures. The T_p values for the COC LCs were determined using a POM images at different temperatures. The sonication times for 60 and 120 s caused dramatic changes in the T_p values obtained by both methods, while sonication times for 300, 900 and 1500 s were causing little changes. The reason for the phase transition may be the dispersion of COC into colloidal particles by effect of ultrasound waves and then the formation of anisotropic self-aggregation. It can be thought that colloidal particles effectively performed this anisotropic self-aggregation for the samples sonicated for 120 s, which in turn the highest phase transition temperature. It has been seen that the change in the sonication time has a effect on temperature of the transition phase. As a result, it was found that the sonication time could change the T_p values and transition phase. These results show that sonication time (which were sonicated for 120s) allows us to control the nucleation-crystal growth balance which will in turn allow to optimize the product and particle properties for future studies

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